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Synthesis and characterization of Metal Ion Imprinted Alginate Network

Girija P[1] and Beena Mathew[2]
[1]*Department of Chemistry, SD College, Alappuzha*
[2]*School of Chemical Sciences, Mahatma Gandhi University, Kottayam,*

ABSTRACT
A novel Mn(II) ion-imprinted interpenetrating polymer network (Mn(II) - IIP was prepared by using alginic acid and NNMBA-crosslinked polyacrylamide. IIP showed higher binding capacity and selectivity than the non-imprinted polymer (NIP). Mn(II)-IIP exhibited good reusability, and the sorption capacity of Mn(II)-IIP was stable.
KEY WORDS: *Biosorption, Ion imprinting, Manganeese,*

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I. Introduction

Molecular recognition is fundamental to the function of biological systems and has great practical importance in advancing science and technology. Naturally occurring biopolymers extracted from algae have been known to exhibit excellent adsorption ability for metal ions [1-2]. Alginic acid which occurs in brown seaweeds is a biopolymer carrying carboxyl groups capable of forming complexes with metal cations. Manganese(II) is a biometal with low contents in natural waters. Lack of this metal in the human organism leads to the bones and cartilages deformation and destroys platelet aggregation [3,4]. The good diversity of procedures concerning the determination of trace levels of Mn, in different matrices, demonstrates the importance of this element. The present paper describes the synthesis, characterisation and selectivity study of NNMBA-crosslinked Mn(II) ion imprinted and non-imprinted interpenetrating polymer networks with high selectivity and specificity.

(i)Materials and methods

Reagents of analytical and spectral grade were used for all experiments. Fourier transform infrared (FTIR) spectra of the metal ion imprinted, non-imprinted, and the Mn(II) ion bound polymers were recorded between 4000-400 cm-1, using a Perkin Elmer 400 FTIR spectrophotometer. SEM-EDAX was taken on JEOL-JSM-840 A Scanning Electron Microscope in nitrogen atmosphere. The amount of metal ion adsorbed was determined before and after binding, using Perkin Elmer Atomic Absorption Analyzer 300.

(ii)Swelling studies

100mg of dried imprinted, non-imprinted polymer and its corresponding Mn (II) bound polymers were allowed to swell in 10 ml water for 24 h. After 24 h the polymers were filtered and surface water was carefully wiped off, and the final swollen weight is determined. From the swollen and the dry weight of the sample the EWC (%) was calculated, using the equation

$$EWC \quad \frac{\text{Weight of wet polymer - Weight of dry polymer}}{\text{Weight of dry polymer}} \times 100$$

(iii)Metal ion binding

In order to investigate specific binding capacity, Mn (II) ion imprinted and non-imprinted polymers investigated towards solutions of Mn (II), Cd(II), Cu(II), Fe(II) and Ni(II) ions by batch equilibration method. The concentration of metal ions before and after binding was determined by AAS.

(iv)Recyclability studies of ion imprinted polymers

In order to investigate the reusability of imprinted polymers of metal ion, it was subjected to several loading (50mg/10mL) of metal ion solution and elution operations. The elution operations were carried out with 4 mL of HCl (3N).

II. Results and Discussions

(i)Synthesis of Mn(II) ion imprinted and non-imprinted polymer networks

The Mn(II) ion imprinted polymer networks were synthesized by free radical polymerization of acrylamide and NNMBA in presence of alginic acid. Potassium persulphate was used as initiator and the polymerisation was carried out at 70^{o}C. The bulk polymer obtained was washed with water to remove unreacted monomers and with dil. HCl to remove Mn(II) ions. The polymer was dried, crushed and sieved. Non-imprinted polymer networks were also prepared without using the template metal ion.

(ii) FTIR Characterization

FTIR spectra of Mn(II) ion imprinted polymer network showed absorption at 1647 cm^{-1} assigned to –COOH group of alginic acid. This band is shifted to 1642cm^{-1} in Mn(II) bound polymer network. The absorptions band at 1455 shifted to 1442cm^{-1-} revealed that -COOH group of alginate is participated in adsorption process. Imprinted polymer showed bands at 2919 cm^{-1} and nonimprinted polymer showed bands at 2922cm^{-1} due to C-H stretching vibrations. IIP showed bands at12422 cm $^{-1}$ and 12626cm^{-1} is shifted to 16393 cm^{-1}and 19531cm $^{-1}$ after adsorption of Mn(II) ion.

(iii) SEM-EDAX

The chemical composition of the polymer networks were confirmed by SEM-EDAX (figure 4). The SEM-EDAX of the metal ion bound polymers showed the presence of Mn(II) ion. The incorporation of Mn(II) ion in metal bound polymer supported the evidence towards the binding of Mn(II) ion.

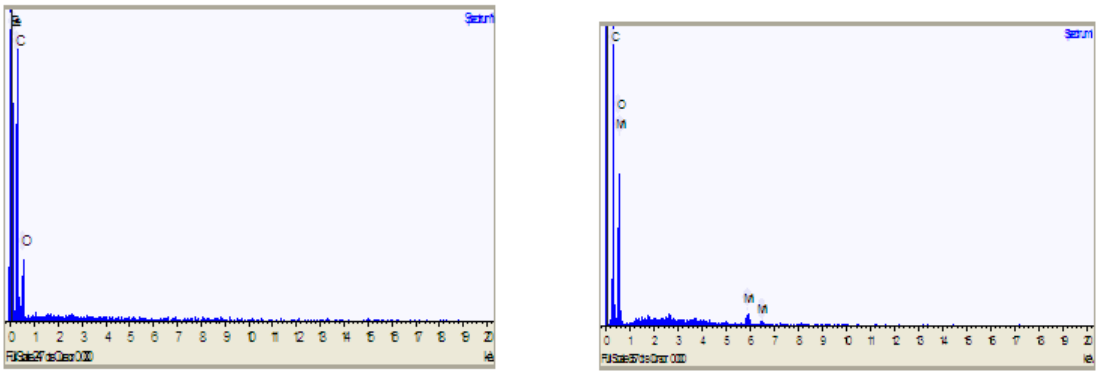

Fig 1. SEM- EDAX of (a) imprinted and , (b) Mn(II) bound polymer

(iv)Swelling studies

Table 1; EWC values of Mn (II) ion imprinted and non-imprinted polymers and their Mn (II) bound polymers

Polymer used	% of EWC
IIP	87.21
NIP	86.10
Mn(II) bound NIP	65.98
Mn(II) bound IIP	69.60

The metal ion binding studies of the polymers in aqueous medium were influenced by the extent of swelling. The swelling behavior of imprinted, non-imprinted polymer networks and the corresponding Mn(II) ion bound complexes were investigated (Table1). Maximum swelling was obtained for Mn(II) ion imprinted polymer. This is due to the adsorption of water in the "pockets" left by the Mn(II) ion. In the case of Mn(II) ion bound polymer networks the swelling decreases due to additional crosslinking which is incorporated on Mn(II) ion complexation

(v)Specificity study

To find out the specific binding of Mn (II) ion, both imprinted and non-imprinted polymer networks were equilibrated with metal ion solutions like Mn (II), Cu(II), Fe(II) and Cd(II) ions. Imprinted polymer showed specificity towards Mn (II) ion.

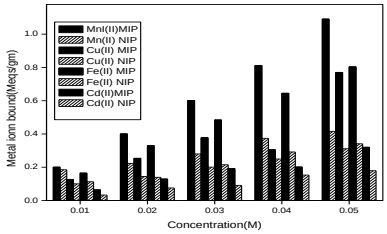

Fig 2. Metal ion binding of iimprinted and non imprinted polymers

The effect of initial concentration of metal ion sorption was investigated by varying the initial concentration of the metal ions (figure-2), such as Mn (II), Cu(II), Cd(II) and Fe(II). It was noted that as the concentration increases, binding of metal ion increases [5-6]. This result could be explained on the basis of a high driving force for mass transfer, where the increase in concentration of metal ion increases the competition to occupy all the available coordination sites in the adsorbent.

(vi) Recyclability studies of ion imprinted polymers

In order to investigate the reusability of imprinted polymers of metal ion, it was subjected to several loading (50mg/10mL) of metal ion solution and elution operations. The elution operations were carried out with 4 mL of HCl (3N). The calculated percentage recovery of the imprinted polymers showed no considerable decrease after six cycles of repeated experiments. The percentage recovery of the recycled IIP could still be maintained at 97% even after repeated cycle of operations.

Table I1. Reusability studies of ion imprinted polymers

Polymer used	**Metal ion sorption capacity in extraction cycles (meq/g)**						
	1	2	3	4	5	6	**Recovery(%)**
Mn(IIP)	0.91	0.91	0.91	0.91	0.90	0.890	97.0

III. CONCLUSIONS

The Mn(II) ion imprinted IIP was synthesised and characterized. Swelling studies proved that maximum EWC is obtained for imprinted polymer. Imprinted polymer showed specificity towards Mn (II) ion. The percentage recovery of the recycled IIP could still be maintained at 97% even after repeated cycle of operations.

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